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Persistent organic pollutants (POPs) as an indicator of surface water quality in the vicinity of the Polish Polar Station, Horsund

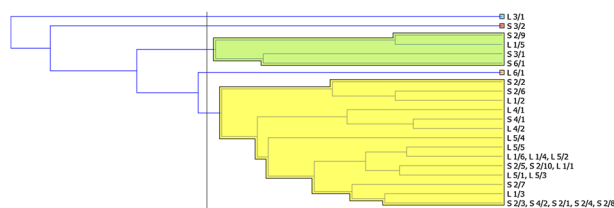
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Abstract

Surface waters were collected in the vicinity of the Polish Polar Station in Hornsund (Svalbard) to determine their concentration of various persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). In addition, parameters such as pH, SEC and TOC were measured. In total, 15 samples of lake water from and 15 samples of stream water were analysed. The sampling took place between August and September 2010. Total PAHs and PCBs concentrations in surface water ranged from < LOD to 6212 ng/dm³ and < LOD to 273 ng/dm³. Moreover, the main compounds detected in the samples from these two groups were naphthalene and PCB 153. Based on the cluster analysis, it was found that there are no significant differences between the water taken from the lakes and the water taken from the streams.

Graphic abstract



Keywords PCB · PAH · Arctic · Spitsbergen · Water

Introduction

The increase in average annual temperature observed in the polar regions in the recent decades is stronger than elsewhere in the world (ACIA 2005), providing a striking example of the global warming effect. Thus, the Svalbard archipelago, which is covered by glaciers in 60%, undergoes various changes caused by the increase of temperature, which affect also its surface waters [1, 2]. Supplying sufficient clean water for growing number of inhabitants and

visitors in the Arctic is an increasingly important concern nowadays.

Though Svalbard is located hundreds of kilometers away from industrial centers, it is not free from pollution. It could have been transported from regions with a temperate climate or produced in the Arctic. The main hypothesis describing the mechanism of long-range pollutant transport to the polar regions is the global distillation. Compounds in a gaseous state or adsorbed on dust particles are transferred along with warm air to the Arctic. Low temperature causes condensation of the chemicals, which leads to their deposition. The local sources of pollution in Svalbard are: heavy industry, tourism, transport and power generators [3, 4]. Climatic conditions occurring in polar regions such as low average annual temperature, low insolation, polar night, snow and ice can influence the durability of chemical compounds present in the Arctic ecosystem. Consequently, they favor

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the accumulation of persistent organic pollutants (POPs). Numerous studies have confirmed that compounds belonging to POPs are present in snow and ice [5–9], and thus melting glaciers may in the future become a secondary source of pollution [10]. In the summer season, Svalbard settlements depend on stream and lake waters for drinking and domestic water supply, and this is also the case for the Polish Polar Station. While the station currently depends on a tundra lake for water supply, it is of interest to know the quality of surface water coming from different sources in the vicinity of the station. Due to the environmental concern connected to POPs, two classes of these were selected as water quality indicators in this work [11].

In this study, compounds belonging to two groups of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were quantified, both groups classified as POPs. The compounds in these groups are carcinogenic or toxic to living organisms, the effect being magnified by their ability to bioaccumulate [12, 13]. As a result, even low concentrations of these compounds in water, sediment and soil are an environmental concern, especially in the case of PCBs, which originate from human activity only. PCBs are mainly used as dielectric fluids and insulating materials. On the other hand, PAHs can be either natural or anthropogenic. The natural sources of emissions include forest fires and volcanic eruptions while the human activities producing them involve the incomplete combustion of fuels and leaks from refineries [14–16].

Results and discussion

While in 20 of the analysed samples naphthalene was detected, only in 6 samples all PAHs were distinguished, and in 4 samples none of these compounds was above the limit of detection (LOD). Total PAHs concentrations in surface water ranged from < LOD to 6210 ng/dm³. The highest concentration of naphthalene (5530 ng/dm³) was found in a sample collected from the lake. In a similar study from 2009, naphthalene was also the most frequently detected compound in the PAHs group [17]. According to WHO guidelines, total PAHs in uncontaminated groundwater (used for drinking water supply) should be in the range 0–5 ng/dm³, yet the contamination may reach as much as 11 µg/dm³ [18]. Hence, the encountered PAH concentrations indicate contamination, but at a relatively low concentration level. The only WHO guideline value for a single PAH compound (benzo[*a*]pyrene, at 0.7 µg/dm³) was not exceeded in any of the considered samples [18]. However, perhaps more appropriate are the EPA guidelines for ambient water quality, with respect to human cancer risk. For the lifetime risk level of 10^{−5}, the total concentration of fluoranthene,

benzo[*a*]pyrene, benzo[*ghi*]perylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and indeno[1,2,3-*cd*]pyrene should not exceed 28 ng/dm³ [19]. By comparing these guidelines to the results obtained, it can be concluded that there is a high level of surface water pollution in the studied area.

In the case of PCBs, mainly high-molecular weight PCBs were detected in these samples (PCB 138, PCB 153, and PCB 180). These compounds were determined at 26 out of the 30 surface water sampling points, at concentrations ranging from < LOD to 273 [ng/dm³]. The highest concentration of any individual PCB (PCB 153; 254 [ng/dm³]) was found in a sample from the lake. With respect to EPA ambient water regulations, the lifetime cancer risk of 10^{−5} corresponds to exposure in ambient waters of 0.79 ng/dm³, however, this guideline takes into account the consumption of freshwater organisms. For the protection of freshwater aquatic organisms, a higher level of 14 ng/dm³ as a 24-h average is deemed sufficient. However, in comparison to these guidelines, the noted PCBs pollution level in the streams and lakes near the Polish Polar Station is causing an environmental concern [20]. Maximum POP concentrations were found in lakes (stagnant water) and thus with respect to this water quality parameter, flowing water seems more recommendable as a drinking water supply (however, it may not always be practical for water supply installations).

The concentration ranges of the tested groups of compounds and parameters are presented in Table 1.

The pH values determined were similar and ranged from 7.24 to 7.89 pH for lakes and from 7.12 to 7.93 for streams. EC was also similar for flowing and stagnant waters, since the measured value for EC was from 49 to 409 µS/cm for lakes and from 37 to 374 µS/cm for streams. These values were similar to measurements carried out elsewhere in Svalbard [20, 21]. The results for TOC showed that more organic carbon was found in samples from the streams (1.75–3.43 mg/dm³) than in samples from the lakes (0.60–2.63 mg/dm³). Table 2 shows the comparison of the results of this study with other published works on surface water on Svalbard.

For parameters such as pH, EC, TOC, total PAHs, and total PCBs, cluster analysis was performed. All parameters except pH have been log-transformed to better represent their distribution. In Fig. 1, a dendrogram is shown which presents the result of the cluster analysis of sampling locations. There are two main clusters, and while the smaller cluster containing 4 samples includes those in which all analyzed compounds from the PAH group were below the detection limit, the larger group contains 23 collected samples. As a result, it can be concluded that the samples taken represent a homogeneous group. In addition, cluster analysis against variables did not show similarities between variables.

Table 1 Concentrations of the tested groups of compounds and parameters at the sampled locations

Object type	EC/ $\mu\text{S cm}^{-1}$	pH	TOC/ mg dm^{-3}	$\Sigma\text{PAH}/\text{ng dm}^{-3}$	$\Sigma\text{PCB}/\text{ng dm}^{-3}$
S2	125–165	7.6–7.93	1.75–3.43	< LOD-3950	< LOD-207.2
S3	37–147	7.12–7.85	2.51–2.54	< LOD-272	< LOD
S4	174–374	7.71–7.75	1.83–2.48	159–760	14.2–73.1
S6	82	7.73	2.14	< LOD	< LOD
L1	113–177	7.36–7.56	1.61–2.37	< LOD-6212	< LOD-88.2
L3	67	7.24	0.60	86	< LOD
L4	372–406	7.65–7.77	1.62–2.64	159–183	0.88–2.7
L5	82–177	7.3–7.78	1.48–1.85	365–3319	19.4–167.4
L6	49	7.89	2.03	2226	273.8
Stream	146 ± 69	7.66 ± 0.20	2.35 ± 0.44	44 ± 65	3.2 ± 2.4
Lake	165 ± 96	7.74 ± 0.18	1.82 ± 0.47	1726 ± 1820	61 ± 78

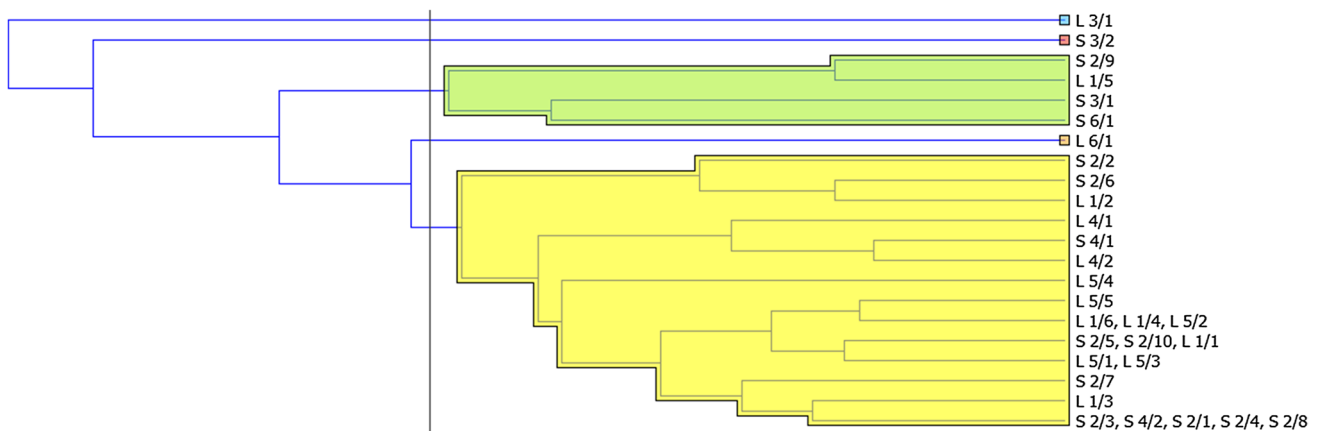
The final two rows show mean \pm 1 standard deviation for streams and lakes

EC electrical conductivity, TOC total organic carbon, ΣPAH total polycyclic aromatic hydrocarbons (16 compounds), ΣPCB total polychlorinated biphenyls (7 congeners)

Table 2 Literature information about the results of the studies of the surface water collected in the Svalbard

Object type	EC/ $\mu\text{S cm}^{-1}$	pH	TOC/ mg dm^{-3}	$\Sigma\text{PAH}/\text{ng dm}^{-3}$	$\Sigma\text{PCB}/\text{ng dm}^{-3}$	Ref
Stream	37–374	7.12–7.93	1.75–3.43	< LOD-3950	< LOD-207	a
Lake	49–177	7.24–7.89	0.60–2.64	< LOD-6212	< LOD-273	
Stream	4.93–7.99	7.59–239	0.11–17.6	–	–	[22]
Lake	5.94–8.21	6.12–228	0.64–2.90	–	–	
Stream	–	–	–	4–600	2–400	[17]
Surface waters	34.5–174.5	6.53–8.50	0.922–2.062	131–3900	–	[23, 24]
Stream	270–287	8.00–8.07	–	–	–	[21]
Lake	184–321	7.54–7.79	–	–	–	
Surface waters	196–342	7.26–8.18	–	–	–	[25]

a this study

**Fig. 1** Result of the cluster analysis of sampling locations. L—lake, S—stream, first number: place of sampling marked on Table 2, second number: ordinal number

Conclusion

The conducted study confirms the presence of compounds from the POP group in the Arctic environment. Higher concentrations of PAHs and PCBs were found in water samples taken from lakes. The source of these compounds cannot be determined due the infrequent detection of the particular PAHs used for indicator ratios. Furthermore, the presence of compounds from the PCB group cannot be attributed only to the effect of global distillation because the Polish Polar Station is located near the sampling area, and in the past these compounds were used in electrical devices which might be the source of their emission. However, it is clear that the detection of such compounds raises a valid environmental concern in this area, especially with respect to aquatic organisms, and should be monitored for long-term trends.

Experimental

Study area

The samples were collected from streams and lakes located in the vicinity of the Polish Polar Station in Horsund. The station is located in the southern part of Spitsbergen on the shores of the Horsund Fjord. Table 3 shows the exact geographical coordinates of the sampling points.

Sampling

Surface water samples were collected in August and September 2010. Fifteen samples of water from streams and 15 water samples from lakes were collected into hermetic containers with a capacity of 1 dm³ made of HPDE. Samples of lakes were collected from at depths 50 cm below water level in a place located 2 m from the shoreline. The stream water was taken from the main stream at depths 20 cm below water level. This was performed with the bottleneck directed towards the water current to prevent the inflow of suspended contaminants. Sampling sites were selected taking into account the morphological and hydrological features of the

watercourses to ensure the representativeness of the whole watercourse or lake.

Reagents and standards

As standard solutions, a mixture of 7 PCBs [PCB 28, PCB 52, PCB 138, PCB 153, PCB 101, PCB 118, PCB 180] in isooctane and a mixture of 16 PAHs (acenaphthylene, acenaphthene, anthracene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene, pyrene) were used, all supplied by Restek Corporation USA. Prior to extraction, four internal standards were injected into the sample [PCB 28 C¹³, PCB 180 C¹³, naphthalene-*d*₈, benzo[*a*]anthracene-*d*₁₂], purchased from Supelco, USA. For liquid–liquid extraction, dichloromethane from Sigma Aldrich, USA, was used.

Instrumentation

For the determination of PCBs and PAHs, an Agilent Technologies 5975C gas chromatograph coupled with an Agilent Technologies 7890A mass spectrometer was used. The analytical column ZB5-MS5 (5% phenyl+95% dimethylpolysiloxane, 30 m×0.25 mm×0.25 μm) provided the separation of analytes, with helium as mobile phase, at a flow rate of 1.3 cm³/min. The temperature programme was the following: initial temperature 40 °C, 40 °C to 120 °C at 40 °C min⁻¹, then 120 °C up to 280 °C at 5 °C min⁻¹, where it was held for 17 min (PAHs) and for 5 min (PCBs). The injection volume selected for all analyses was 2 mm³, injection mode: splitless. The mass spectrometer was operated in the selected ion-monitoring (SIM) mode. We have added new information about the method and QA/QC. The following mass to ion ratios were monitored: PAH: *m/z* = 128, 127, 152, 151, 153, 154, 166, 165, 178, 176, 203, 202, 228, 226, 252, 250, 277, 276, 278, and 279, and for PCB: *m/z* = 256, 258, 290, 292, 234, 326, 358, 360, 392, and 394. Before sample analysis, the relevant standards were analysed to check column performance, peak height and resolution, and the limits of detection and quantification. A solvent blank, a standard mixture and a procedural blank were run in each sequence of samples to check for contamination, peak identification and quantification. This way, the background level present in the reagents and analytical containers used during the analytical procedure could be eliminated. Average recoveries of standards in the following validation studies were in the range: 70–85%, and the recoveries of internal standards were 80%, 85%, 82% and 80%, for naphthalene-*d*₈, benzo[*a*]anthracene-*d*₁₂, PCB 28 C¹³, and PCB 180 C¹³, respectively. A CV unit has also been added.

Table 3 Geographical coordinates of the sampling points

Locations	Latitude	Longitude
1	77°0'22.3"N	15°33'12.522"E
2	77°0'22.35"N	15°32'48.415"E
3	77°0'44.808"N	15°25'59.295"E
4	77°0'31.13"N	15°34'7.148"E
5	76°59'56.39"N	15°29'58.67"E
6	77°1'51.359"N	15°29'37.285"E

Table 4 Measurement ranges of analytical methods used

Analytes/parameters		Measuring range	LOD	LOQ	CV/%
PCBs ^a		0.02–560	0.025	0.075	0.5–5
PAHs ^a	Naphthalene	0.034–560	0.034	1.02	0.5–5
	Acenaphthylene	0.0041–560	0.0041	0.0123	
	Acenaphthene	0.0041–560	0.0041	0.0123	
	Fluorene	0.0018–560	0.0018	0.0054	
	Phenanthrene	0.0025–560	0.0025	0.0075	
	Anthracene	0.0078–560	0.0078	0.0234	
	Fluoranthene	0.014–560	0.014	0.042	
	Pyrene	0.028–560	0.028	0.084	
	Chrysene	0.0022–560	0.0022	0.0066	
	Benzo[b]fluoranthene	0.014–560	0.014	0.042	
	Benzo[k]fluoranthene	0.0023–560	0.0023	0.0069	
	Benzo[a]pyrene	0.0055–560	0.0055	0.0165	
	Benzo[a]anthracene	0.0017–560	0.0017	0.0051	
	Indeno[1,2,3- <i>cd</i>]pyrene	0.43–560	0.43	1.29	
	Dibenz[<i>a,h</i>]anthracene	0.014–560	0.014	0.042	
TOC ^b		0.030–10.00	0.030	0.100	0.1–0.5
pH		0–14	–	–	0.4
EC ^c		0.0000001–2	–	–	0.5

^ang/dm³; ^bS/cm; ^cmg/dm³

The TOC determination was performed using catalytic oxidation with oxygen at 680 °C, with non-dispersive infrared spectroscopy as detection method, on a Total Organic Carbon Analyser TOC-VCSH/CSN (Shimadzu). The measurements of pH and electrical conductivity (EC) were performed with a microcomputer pH-meter and conductivity meter (inoLab® Multi 9310 IDS pH), equipped with a Tetra-Con® 925 conductivity sensor and a SenTix®940 electrode. Table 4 shows the LOD, the limit of quantification (LOQ), concentration ranges and parameters of the determination methods applied in this work.

Sample preparation

Prior to analysis, the PCBs and PAHs 500 cm³ water samples were spiked with internal standards (PCB 28 C¹³, PCB 180 C¹³, naphthalene-*d*₈, benzo[*a*]anthracene-*d*₁₂). A two-stage liquid–liquid extraction with dichloromethane was then carried out. After each addition of 15 cm³ dichloromethane, the samples were shaken for 30 min, and the extracting solvent was transferred into a glass vial. Lastly, the extracts were evaporated to a volume of approximately 1 cm³ in a gentle stream of nitrogen.

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